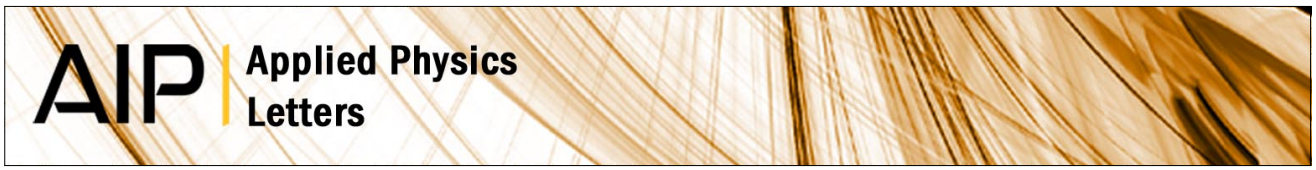

a-Si nanolayer induced enhancement of the 1.53μm photoluminescence in Er3+ doped a-Al2O3 thin films

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a-Si nanolayer induced enhancement of the 1.53 μm photoluminescence in Er^{3+} doped *a*-Al_2O_3 thin films

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A structured film formed by an active Er^{3+}-doped amorphous Al_2O_3 layer located between two amorphous silicon nanolayers (NLs) in as-grown conditions shows an enhancement of the photoluminescence (PL) intensity and lifetime at 1.53 μm of one order of magnitude when compared to a similar Er^{3+}-doped film without silicon NLs. The film can be pumped even under nonresonant excitation conditions as a result of a long range energy transfer from the *a*-Si NLs to the Er^{3+} ions. In addition, the PL shows a single exponential decay with a lifetime value as high as 2.4 ms. The lifetime enhancement is associated with an improvement of the emission efficiency of the Er^{3+} ions. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2900662]

In scaling down the system dimensions to substitute the Er-doped fiber amplifier by waveguide amplifiers integrated on silicon platforms with lateral dimensions of a few microns, it has become mandatory to design thin films displaying an intense 1.53 μm Er^{3+} photoluminescence (PL) and a long lifetime for the corresponding excited state. Enhancing the PL intensity requires to maximize the number of active ions and to limit the efficiency of nonradiative decay channels, for instance, by minimizing clustering and concentration quenching, respectively. The influence of such unwanted phenomena can be significantly reduced by controlling the Er^{3+} ion distribution within the material at the nanoscale.[1,2] An enhancement of the PL intensity can also be achieved by maximizing the radiative decay rate of the emitters. According to Fermi's golden rule,[3] this can be done by tuning the local density of optical states (LDOS), thus, inducing changes in the probability of the radiative decay processes as it has been shown in several works, for instance, by locating the emitters close to interfaces between various media,[4–7] or in Si/SiO_2 multilayers with a tailored nanostructure.[8] Alternatively, it has been proposed that a modification of the LDOS also influences the nonradiative decay processes.[9,10] Important improvements of the PL efficiency of Er-doped materials (usually Er-doped SiO_2) can also be realized by incorporating sensitizers [such as Si nanoparticles[11,12] or Si nanolayers[13–15] (NLs)] in order to overcome the low absorption cross section of Er^{3+} ions.

In previous works, Er-doped amorphous aluminium oxide (*a*-Al_2O_3) films with a nanoscale-controlled Er in-plane concentration and in-depth distribution have been prepared by alternate pulsed laser deposition (PLD) to achieve an improved PL performance.[1,2] The aim of this work is to get a further enhancement of the PL response of the Er^{3+} ions in these films by incorporating silicon nanostructures which can induce both a sensitizing effect and a modification of the Er^{3+} decay rate.

An ArF excimer laser ($\lambda=193$ nm, $\tau=20$ ns, 5 Hz, ~ 2 J cm^{-2}) was used to alternatively ablate independent Al_2O_3, Si, and Er targets to grow the films on Si substrates held at room temperature. The film structure, which can be schematically described as *a*-Al_2O_3/*a*-Si/Er^{3+}:*a*-Al_2O_3/*a*-Si/*a*-Al_2O_3 (Si/Er:Al_2O_3/Si film hereafter), is shown in Fig. 1. The central *a*-Al_2O_3 layer consists of 50 Er-doped layers separated by 5 nm leading to an average Er concentration of 10^{20} cm^{-3}.[1,2] The first and the last Er-doped layers are designed to be separated from the *a*-Si NLs by 8 nm thick *a*-Al_2O_3 layers. The *a*-Si NLs are 6 nm thick and the *a*-Al_2O_3 buffer layers on top and below are 52 nm thick. Spectroscopic ellipsometry measurements show good agreement with this intended design within 2%.[16] The thickness values of the nanostructured film have been chosen to minimize its reflectance in the pumping conditions of our PL setup.[16] An Er-only doped reference film (Er:Al_2O_3) prepared in similar conditions, i.e., with the same total thickness and Er doping but without *a*-Si NLs, shows a reflectance close to 0.40, while that for the Si/Er:Al_2O_3/Si film is 0.05 at 514.5 nm.[16] The PL response has been pumped with an Ar^+ ion laser (S polarized, power of 70 mW) at an incidence angle of 25° with the sample normal. The PL signal was detected at room temperature along the direction perpendicular to the film by using a monochromator, a Hamamatsu near-infrared photomultiplier tube module, and standard lock-in techniques.

The PL response of the films has been studied in as-grown conditions, i.e., without performing any thermal annealing. This is different from earlier studies in which the

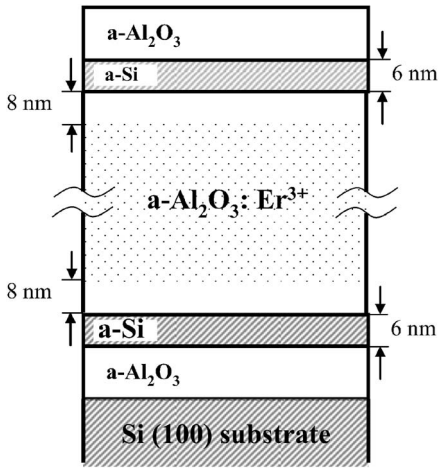

FIG. 1. Schematic representation of the Si/Er:Al_2O_3/Si film structure. It is not to scale in order to show the most relevant parameters of the structure.

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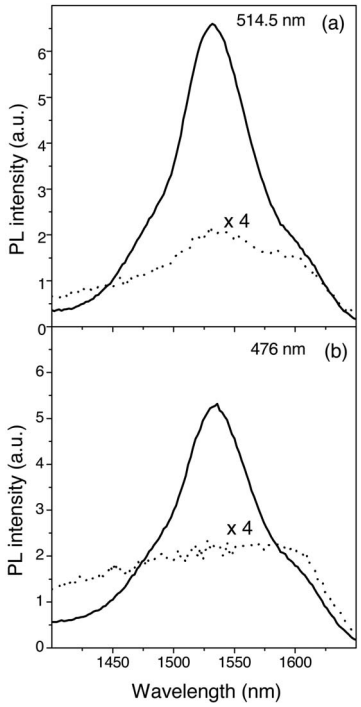

FIG. 2. PL spectra of the $Si/Er:Al_2O_3/Si$ (full lines) and $Er:Al_2O_3$ (dotted lines) films (a) under excitation at 514.5 nm and (b) under excitation at 476 nm. The spectra corresponding to the $Er:Al_2O_3$ film have been magnified by a factor of 4.

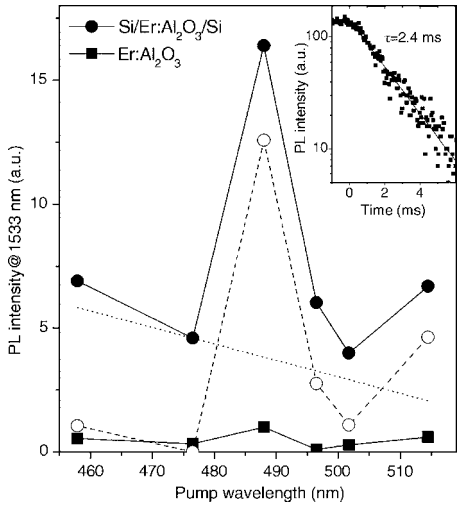

FIG. 3. Excitation spectra of the $Si/Er:Al_2O_3/Si$ (full circles) and $Er:Al_2O_3$ films (full squares). The estimated contributions of indirect (dotted line) and direct (open circles, dashed line) excitations are also shown. The inset shows the measured PL decay curve for the $Si/Er:Al_2O_3/Si$ film under excitation at 514.5 nm (dots) and the corresponding best fit (full line).

Er-doped Al_2O_3 films have been annealed at high temperature[1,2] and from most of the works dealing with silica based materials.[11–15] Figure 2 shows the PL spectra obtained for the films when pumping at 514.5 nm [Fig. 2(a)] and 476 nm [Fig. 2(b)], i.e., in resonant and nonresonant excitation conditions for the Er^{3+} ions. When pumping at 514.5 nm, the emission band characteristic of the Er^{3+} luminescence with a maximum at 1533 nm can be seen for both films due to excitation at the Er^{3+} $^4I_{15/2} \rightarrow {}^4F_{7/2}$ transition. Nevertheless, the maximum PL intensity is one order of magnitude higher for the $Si/Er:Al_2O_3/Si$ film. Under pumping at 476 nm, a strong Er^{3+}-related PL band is observed for the $Si/Er:Al_2O_3/Si$ film; however, no Er^{3+}-related PL band is observed for the $Er:Al_2O_3$ film. This suggests that the *a*-Si NLs act as sensitizers providing efficient excitation of the Er^{3+} ions in nonresonant excitation conditions.

Further evidence of this phenomenon is given by the excitation spectrum of the $Si/Er:Al_2O_3/Si$ film presented in Fig. 3. Indeed, it shows a high Er^{3+} PL intensity at the nonresonant excitation wavelengths of 459.7 and 501.7 nm, at which no Er^{3+}-related PL is observed for the $Er:Al_2O_3$ film. The excitation spectra of materials whose PL is induced by energy transfer from silicon sensitizers to Er^{3+} ions are usually nearly independent of the pumping wavelength.[14] Nevertheless, in the case of the $Si/Er:Al_2O_3/Si$ film, a clear maximum of the Er^{3+} PL intensity is observed for the resonant excitation wavelength of 488 nm which reflects the $^4I_{15/2} \rightarrow {}^2H_{11/2}$ optical absorption of Er^{3+}. This evidences that in addition to indirect pumping through the *a*-Si NLs, there is also a significant contribution to the measured PL intensity due to direct in-band optical Er^{3+} excitation. To evaluate the contributions of the direct and indirect processes to the excitation spectrum of the $Si/Er:Al_2O_3/Si$ film, we have assumed the direct contribution to be negligible at 476 nm and to have a similar value at 459.7 and 501.7 nm (as in Ref. 14 for $SiO_2:Er$). By subtracting this direct contribution to the measured PL, the indirect contribution for these three wavelengths has been obtained and it leads to a linear slightly decreasing function (see Fig. 3), in good agreement with the decrease of the *a*-Si absorption as a function of wavelength in the 460–520 nm range. Therefore, it has been assumed that this linear function accounts for the indirect contribution in the whole studied wavelength range, and taking it into account, the direct contribution has been estimated at 488, 496.5, and 514.5 nm and plotted in Fig. 3. It is seen that the indirect excitation is the dominant process at 457.9, 476.5, and 501.7 nm and is responsible for 25% and 30% of the total PL at 488 and 514.5 nm, respectively. Moreover, it is shown that the PL arising from directly pumped ions in the $Si/Er:Al_2O_3/Si$ film is still one order of magnitude more intense than the PL of the $Er:Al_2O_3$ film (see excitation spectrum in Fig. 3).

Therefore, from the above discussion, it seems that the *a*-Si NLs in the $Si/Er:Al_2O_3/Si$ film induce two different phenomena both contributing to the enhancement of the Er^{3+}-related PL. The first one is a sensitizing effect involving energy transfer from the *a*-Si NLs to the rare-earth ions. This is an unexpected result since the *a*-Al_2O_3 layer thickness separating the *a*-Si NLs from the first Er-doped layer is 8 nm and the known energy transfer processes between Si sensitizers and Er^{3+} ions strongly decrease with distance.[13–15] Indeed, previous reports have claimed a maximum value of 2 nm for the interaction length between *a*-Si NLs and Er^{3+} ions in $Er:Si:SiO_2$ films.[15] A contamination of the *a*-Al_2O_3 spacing layer with Er and Si, which would allow a shorter interaction length, is very unlikely since the PLD deposition from separate targets has shown to always lead to sharp interfaces for X/Al_2O_3 multilayers (X=Er, Cu, Ag, Si).[1,2,17–19] Thus, assuming negligible Er and Si contamination in the 8 nm Al_2O_3 spacing layer, it can be proposed that an energy transfer mechanism different from that in the case of the $Er:Si:SiO_2$ films might be involved. Two different mechanisms are effectively known to permit the energy transfer from silicon nanostructures to Er^{3+} ions:[15,20] a short-range and fast Auger exchange process related to intraband transitions of confined electrons and holes in silicon[15] and a slower

process involving the recombination of excitons and a Förster dipole-dipole interaction with rare-earth ions.[20] The latter mechanism, which has been shown to allow an efficient energy transfer from InGaN NLs to CdSe nanoparticles separated by 5 nm,[21] might occur in our case. Further investigations are on the way.

The second phenomenon contributing to the improved PL of the $Si/Er:Al_2O_3/Si$ film is evidenced from the strong enhancement of the PL intensity of the directly pumped Er^{3+} ions due to the presence of the *a*-Si NLs. From the lower reflectance of the $Si/Er:Al_2O_3/Si$ film when compared to the one of the $Er:Al_2O_3$ film, an enhanced effective excitation of the Er^{3+} ions in the active $Er^{3+}:Al_2O_3$ region could be expected. Nevertheless, calculations of the in-depth profile of the pump electric field (based on the Abélès matrix formalism) show that the effective direct pumping of the Er^{3+} ions is similar in both films. Note that although the reflectivity of the $Si/Er:Al_2O_3/Si$ film is reduced, there is a significant absorption of light by the *a*-Si NLs in the visible that reduces the pump light that reaches the active $Er^{3+}:Al_2O_3$ region. Therefore, the observed PL enhancement seems to be due to an improvement of the emission efficiency of the rare-earth ions, which is reflected by the measured lifetime. The inset of Fig. 3 shows the PL decay curve of the $Si/Er:Al_2O_3/Si$ film pumped at 514.5 nm which has been fitted with a single exponential function corresponding to a lifetime value $\tau=2.4$ ms. This value is significantly longer than the one for the $Er:Al_2O_3$ film, whose decay time is below 0.5 ms, in agreement with our earlier reports which show that annealing up to 700 °C is necessary to obtain lifetime values in the millisecond range for the $Er^{3+}:Al_2O_3$ PLD films.[1,2] At this point, the origin of this lifetime increase is uncertain, although it is obviously linked to the presence of the *a*-Si NLs which might, on the one hand, be responsible for a modification of the LDOS at the emission wavelength, thus, modifying the radiative lifetime τ_r. On the other hand, for a given number of active ions and pumping power, the PL intensity I and lifetime τ of directly pumped ions are linked by the relation $I \propto \phi N \sigma_{abs} \tau / \tau_r$ with $1/\tau = 1/\tau_r + 1/\tau_{nr}$, where ϕ is the photon pump flux, N is the density of active Er^{3+} ions, σ_{abs} is the pump absorption cross section, and τ_{nr} is the nonradiative component of the lifetime. Therefore, for films with the same Er concentration and under the same measuring conditions for direct pumping, the PL intensity is $I \propto (1+\tau_r/\tau_{nr})^{-1}$. Hence, a simultaneous enhancement of τ and PL intensity, as observed for the directly pumped ions in the $Si/Er:Al_2O_3/Si$ film, implies that the nonradiative lifetime τ_{nr} should increase. It has previously been reported that as-grown $Er^{3+}:Al_2O_3$ films prepared by PLD at room temperature show a relatively low PL intensity and a short lifetime, and this has been ascribed to the presence of a high density of defects that allow fast nonradiative recombination routes and, thus, quench the PL.[2,22] An improvement of the PL response of such materials, therefore, requires either decreasing the number of nonradiative decay channels, which is commonly achieved by annealing the films to remove the defects,[22] or alternatively as it seems in this case, decreasing the probability of nonradiative processes which could be affected by the LDOS, as discussed in several works.[9,10] Nevertheless, this interpretation needs a more detailed investigation since the role of the LDOS on nonradiative processes is not fully understood. More precisely, in Ref. 7, it is shown that nonradiative processes are not affected by the LDOS at the emission wavelength of the Er^{3+} ions, in contradiction with the interpretation of the results in Ref. 10. However, the authors in Ref. 7 also suggest that a broad spectral variation of the LDOS in the emitters region could explain results such as those reported in Ref. 10 and in our case. A complete calculation of the LDOS between the silicon layers, which lies outside of the scope of the present work, could enlighten this issue.

Summarizing, a nanostructured $Si/Er:Al_2O_3/Si$ film with a low reflectance and an optimized ion distribution has been prepared by PLD. This structure in as-grown conditions shows a significant enhancement of the PL intensity and lifetime of the Er^{3+} ions when compared to a similar film without *a*-Si NLs. The *a*-Si NLs in the nanostructure seem to play a double role: they act as sensitizers for the Er by providing a long range energy transfer to the rare-earth ions and they lead to an improvement of the emission efficiency of the Er^{3+} ions. Therefore, it has been possible to produce films with efficient Er-related PL by a single step process at room temperature without the need of further processing, opening a possible route for the production of low cost devices.

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